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A Simple Reliable Method for the Determination of Airborne Hexavalent Chromium

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A method is presented to determine airborne hexavalent chromium concentrations. Samples collected on polyvinyl chloride membrane filters have good long term stability and are easily washed clean so that a colorimetric determination with diphenylcarbazide can be performed up to two weeks after the time the sample was originally collected.

Introduction

THE NATIONAL INSTITUTE FOR Occupational Safety and Health (NIOSH) undertook a study to develop a method for the reliable determination of airborne mists of hexavalent chromium. An estimated 90,000 workers in this country are exposed to this substance at various worksites including chrome plating plants, bichromate production plants, metal works, and the dye and paint industry. The acceptable ceiling value is 0.1 mg CrO_3/m^3 according to the current Occupational Safety and Health Act (OSHA) standard. See Table G2 of the October 18, 1972 Federal Register.[1] In addtion to the ceiling value, a time weighted average value of 0.05 mg CrO_3/m^3 for chromic acid mists is now being proposed by NIOSH.[2] The OSHA standards for other soluble and insoluble chromium compounds are 0.5 and 1.0 mg/m^3 respectively and it is therefore necessary to measure specifically for hexavalent chromium.

In the past samples have been collected in impingers with a sodium hydroxide absorbing solution or water. Various filter and wool plug materials have also been used in air sampling. Most methods utilized the reagent *s*-diphenylcarbazide which reacts specifically with hexavalent chromium, Cr(VI), to form a colored complex. This technique has been used for about 75 years.[3,4] Other methods make use of the color of CrO_4^{-2} itself,[5] the violet color produced with hematoxylin,[6] precipitation methods, or the oxidizing power of Cr as measured by iodine generation and thiosulfate titration.[7]

In 1947 Ege and Silverman[8,9] reported work on a colorimetric method for the determination of Cr(VI). In part of the work they impregnated filter papers directly with *s*-diphenylcarbazide and used the intensity of the color after exposure to hexavalent chromium as a rapid method of assessing its concentration in the air.[8] In a study of the efficiency of filter papers and impingers, they analyzed filter papers by washing with water and adding *s*-diphenylcarbazide to the wash[9] which is essentially the method described in this paper. They found, however, that if filter papers are used for field sampling and allowed to stand for any period of time before analysis, it is necessary to oxidize the sample to hexavalent chromium in order to be able to make the analysis.

Sampling procedures employing impingers

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are cumbersome and make the collection of breathing zone samples difficult. In addition, impingers suffer from low and variable collection efficiency as indicated in work done at NIOSH on the efficiency of impingers as compared to the essentially 100% efficiency of membrane filters.[10] This great efficiency advantage of filters is the important conclusion here, however, and was verified in the study of Ege and Silverman.[9]

When the analytical methods are judged on the basis of sensitivity and specificity, the *s*-diphenylcarbazide-colorimetric procedure is the logical choice. Placing the *s*-diphenylcarbazide on the filter before sampling gave Ege and Silverman[8,9] a rapid method of estimating Cr(VI), but the results were not highly consistent with their impinger results (usually lower) and were for test concentrations above the OSHA standards. Their method of washing a filter after sampling and then adding *s*-diphenylcarbazide could not be used to determine hexavalent chromium in the presence of other forms since the papers that they used had a tendency to reduce the Cr(VI). In our earlier work, cellulose membrane filters were used to sample Cr and discoloration of the filter was obvious within a few hours, indicating that a reaction was taking place on the filter. Others have observed this instability problem.[11]

Since the polyvinyl chloride (PVC) filter did not seem to react with the Cr(VI), it was decided to test the method of sampling with a PVC filter, washing the filter to remove the Cr(VI) and adding *s*-diphenylcarbazide to the wash for the colorimetric determination. The resulting simple method is reported below.

Reagents and Apparatus

The water used in making reagents is double deionized water having a specific resistance of 18 megohom-cm or higher. The reagents are ACS reagent grade.

Sulfuric acid wash solution: Dilute 13.8 ml of concentrated H_2SO_4 to one liter with water. After mixing, put some of this solution into a small plastic squeeze bottle for easy use in the washing procedures.

s-Diphenylcarbazide solution: Dissolve 0.5 gram of 1,5-diphenylcarbohydrazide in 200 ml of 1:1 acetone-water. Store in a dark bottle in the refrigerator. Make fresh once a month.

Chromium (VI) standard: Dissolve 0.2826 g of $K_2Cr_2O_7$ in water and dilute to one liter. This solution contains 100μg of Cr(VI) per ml.

A Beckman Model B spectrophotometer was used for most of the tests run in this laboratory, but any equivalent spectrophotometer may be used. Large (22 x 150 mm) matched test tubes from Bausch and Lomb were used as sample cells. Cells of this size provide adequate sensitivity. These cells were calibrated by pipetting 15 ml of water into each and using the edge of a piece of tape to mark the meniscus.

Filtration was facilitated by enlarging one hole of a #5 two-hole stopper to accommodate a small Buechner funnel (Coors size No. 0) and placing a piece of glass tubing bent to 90° in the other hole for the vacuum line. This stopper will fit the top of the 22 mm cells. Other necessary apparatus includes large test tubes, stirring rods, micropipets and a small forceps with teflon coated tips for handling the filters.

Procedure

A PVC filter (5μm pore size, Gelman VM-1) was used for sampling. In the field, a 37-mm filter was placed in a cassette which is attached to a worker's collar and a battery operated 2-liter-per-minute pump. For determinations near the OSHA standard, about 100 liters of air are required. The filters can be stored in the cassettes for up to two weeks. In the laboratory, the filter was removed from the cassette with forceps and crumpled in the bottom of a large test tube using a stirring rod. The background level of Cr(VI) in unused filters from the same batch was checked.

Using the squeeze bottle, 5 or 6 ml of the sulfuric acid washing solution were placed in the tube and the tube swirled to promote complete mixing. After one minute the filter was removed from the tube; it was pulled up to the side with the stirring rod and held over the top of the tube with forceps and washed with a stream of the acid solution from the squeeze bottle (several ml.).

Any dust was removed from the wash in the tube by filtering through another PVC filter. With the aparatus described above, the wash could be filtered directly into the large colorimetric cells. Additional acid solution was used to wash the filtering apparatus. Standards were begun at this point by pipetting increasing amounts of the 100 μg/ml Cr(VI) standard solution into successive matching cells that already contained 5 or 6 ml of the H_2SO_4 acid washing solution. The amounts used ranged from 5 μl which contains 0.5 μg Cr(VI) up to 100 μl which contains 10.0 μg Cr(VI). At this point, 0.5 ml of the *s*-diphenylcarbazide solution was added to all cells followed by additional acid washing solution from the squeeze bottle to each of the cells to bring the final volume to the tape mark mentioned above; thus each cell contained 15 ml.

The tubes were swirled to mix the contents and the outside wiped clean. Color development is fast (complete within two minutes), but ten minutes should elapse before the color is measured if vanadium interference is possible. The spectrophotometer was set for use at 540 nm and zero absorbance was set using the H_2SO_4 wash solution and 0.5 ml of *s*-diphenylcarbazide (with no Cr(VI)). The absorbance was read for all the cells. From the plot of the absorbance as a function of micrograms of Cr(VI) for the standards, the number of micrograms of Cr(VI) for each of the samples was determined. The background (filter blank) was negligible, otherwise its value in micrograms of Cr(VI) would have been subtracted from each sample value at this point. In the discussion below, results for artifically generated samples are reported as μg Cr(VI) per filter for simple comparison. For comparison to the OSHA standard, results in μg Cr(VI) per filter can be multiplied by 1.92 (the gravimetric factor relating CrO_3 to Cr) to obtain μg CrO_3 and this can be divided by the number of liters of air sampled to give mg CrO_3/m^3. The field samples discussed below are reported in μg CrO_3/m^3 because of the very low concentrations.

Discussion

The *s*-diphenylcarbazide methods is very sensitive; using the 22-mm cells with 15 ml of solution gives a sensitivity (for 1% absorption) of 0.04 μg of Cr(VI). The calibration curve for the colorimetric procedure is linear up to 15 μg Cr(VI) (1 ppm in the solution) which is about 29 μg CrO_3. The calibration curve is shown in Figure 1. The interferences from iron, copper and nickel were found to be negligible. If vanadium is present, a high absorbance reading will be obtained for a sample measured immediately. However, if the absorbance is measured after ten minutes from the time of adding the *s*-diphenylcarbazide, this positive interference of vanadium is negligible up to a 100-fold excess. The absorbance for standards that do not contain interfering elements

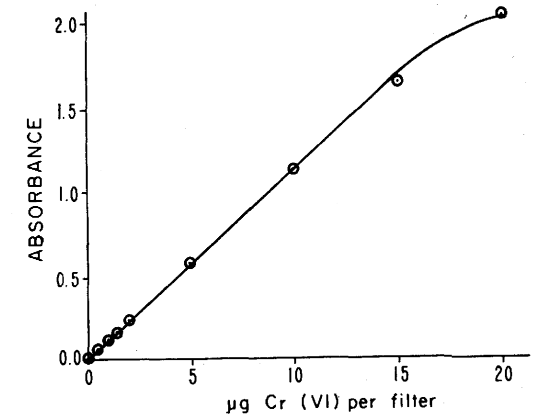

Figure 1. A calibration curve showing the working range when the 22-mm cells described are used. The absorbance of the Cr(VI) diphenylcarbazide complex is plotted as a function of the total amount of Cr(VI) present.

decreases by approximately 5% of its original value after one hour. It is not recommended to wait this long to make a measurement since the absorbance of samples may decrease more rapidly depending on the other materials present.

Of primary concern was the stability of the samples on the filter paper. Placing a droplet of Cr(VI) solution ($K_2Cr_2O_7$) on a PVC filter and allowing it to dry did not produce a very stable sample. In fact, when these spiked filters were analyzed within an hour of deposition, the recovery was greater than 90%, but after one week the recovery was about 50%. Filters prepared in a mist generator were more stable.

A mist generator was constructed in the NIOSH Engineering Branch and is fully described by Carson and Murdock.[10] The generator consists mainly of a nebulizer at the bottom of a vertical plexiglass chimney which has six sampling ports near the top. Three of the sampling ports were set up for impinger sampling and three used for filter sampling. Table I shows the results in μg Cr(VI) for filters exposed to Cr(VI) in the mist generator at the indicated ports on successive closely controlled runs. The results for each port are averages for several filters analyzed one day, one week or two weeks after generation, with a total of 22 filters having been analyzed.

TABLE I
Average Values of Hexavalent Chromium (μg/filter) Collected from the Mist Generator and Analyzed after the Number of Days Shown.

	1 day	7 days	14 days
Port 4 filters	5.34	5.26	5.14
Port 5 filters	6.05	5.67	5.64
Port 6 filters	5.66	5.62	5.63

Since the PVC filter seemed to be a good substrate for collecting stable samples, the next obvious question was the effect of other materials collected along with the easily reduced Cr(VI). As an indication of contaminant interference, PVC filters that had previously been used to collect 0.4 mg of coal dust and then exposed to Cr in the mist generator were analyzed. The results after three days' storage showed about 3.4 μg Cr(VI) per filter, whereas the results after two hours had been 4.3 μg Cr(VI). Blank values of Cr(VI) in the coal dust were variable but all were quite low as compared to these values. These results under very adverse conditions indicated that a field test would be worthwhile.

Field samples were collected at a chrome plating plant on a manifold that held six filters in close proximity. For each run, four PVC and two cellulose membrane filters were monuted on the manifold. The purpose of the cellulose filters was to monitor total Cr during the test, cellulose filters being easily wet ashed and analyzed by atomic absorption spectrophotometry (AAS). There were four runs. Table II shows the results in μg CrO_3/m^3 for three of the four runs, each number here representing the analysis of only one filter.

The results of Run 2 are not shown in Table II because the limited worker activity in the plant at the time of Run 2 resulted in very low Cr(VI) levels. It is partly because of the low level of Cr(VI) for all the runs that the data show wide variability, but the data also show that there is not a general tendency for Cr(VI) to degrade to Cr(III) in actual samples when PVC filters are used. About 150 liters of air were sampled in Runs 1 and 3 and about 400 liters of air were sampled in Run 4.

TABLE II
Airborne Hexavalent Chromium Concentration (μg CrO_3/m^3) in a Chrome Plating Plant as Determined from PVC Filters Used in Three Sample Runs
(Number of days indicated is time elapsed between sampling and analysis.)

	2 days	2 days	7 days	14 days
Run 1	8.9	11.0	8.1	9.5
Run 3	5.9	6.4	5.6	3.3
Run 4	4.9	4.9	5.4	6.0

After these samples were analyzed colorimetrically, the same solution was aspirated into an atomic absorption spectrophotometer to detect total chromium. The sulfate rich medium of the wash quenched the Cr absorption causing low sensitivity, but the results showed the total chromium to agree well with that determined by AAS analysis of the wet-ashed cellulose membrane filters. The values were two to three times higher for total chromium (See Table III) than for Cr(VI) (Table II). This is not surprising in view of the plant process involved; objects plated in the chromic acid bath were then immersed in sodium bisulfite solution which changed Cr(VI) to Cr(III) and then the objects were suspended in air and washed with water from a shower head.

The reproducibility of the washing and analysis portion of the procedure as determined with spiked filters was 3% relative standard deviation. However, since these spiked filters had been observed to have poor stability, the meaning of this number was not clear even though the filters had been analyzed within an hour of spiking. The data in Table I are for 22 filters from the mist generator. When the data from the three ports are pooled, a relative standard deviation of 4.3% results. It should be noted that some of the 22 samples were analyzed one and two weeks after others.

Conclusion

The method given here has the advantage of being very simple, specific and sensitive for hexavalent chromium. PVC filters are used for sampling and are washed in a dilute acid solution. This wash is analyzed for Cr(VI) with the colorimetric reagent *s*-diphenylcarbazide. This is not a new method except for the use of the PVC filters which have the advantage of retaining the chromium in the hexavalent state for up to two weeks. Filter materials that reduce the Cr(VI) or do not allow it to be washed out would be unsatisfactory. The PVC filter allows a test that is specific for hexavalent chromium, a condition that permits evaluating compliance with the OSHA standard for that substance.

TABLE III

Total Airborne Chromium Concentration ($\mu g\ CrO_3/m^3$) as Determined from Individual PVC or Cellulose Filters from a Chrome Plating Plant

(Number of days indicated is time elapsed between sampling and analysis.)

	PVC filters*				Cellulose filters	
	2 days	2 days	7 days	14 days	2 days	14 days
Run 1	16	17	16	14	17	18
Run 3	12	16	16	17	25	20
Run 4	16	17	15	17	16	18

*These filters were washed to obtain the Cr(VI) values of Table II and then this same wash aspirated into an AA spectrophotometer to obtain these total chromium values.

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References

1. ....: Federal Register, Vol. 37, No. 202, Part II, p. 22140 (29CFR 1910.93).
2. ....: *Exposure to Chromic Acid Mist; A Recommended Standard,* (HSM 73-11021).
3. Cazaneuve, P.: *Bull Soc Chem, 23:*701 (March 1900).
4. Ege, J. F., Jr., and L. Silverman: A Stable Colorimetric Reagent for Chromium. *Ind. & Eng. Chem., Anal Ed, 19:*693 (Sept. 1947).
5. Sandell, E. B. *Colorimetric Determination of Traces of Metals.* Third Edition, pp. 388 & 390, Interscience Publishers, New York (1959).
6. Jacobs, M. B.: *Analytical Chemistry of Industrial Poisons, Hazards and Solvents.* p. 207, Interscience Publishers, New York (1941).
7. *Ibid.,* p. 206
8. Ege, J. F., Jr., and L. Silverman: A Rapid Method for the Determination of Chromic Acid Mist in Air. *J. Ind. Hyg. & Toxicol. 29:* 136 (1947).
9. Ege, J. F., Jr., and L. Silverman: Efficiency of Filter Paper and Impingers for Chromic Acid Mists in Air. *Amer. Ind. Hyg. Assoc. Quart. 8:* 12 (March 1947).
10. Carson, G., and D. Murdock: Generation of Chromic Acid Mist for Sampling Method Evaluation. *Amer. Ind. Hyg. Assoc. J.* In press.
11. Dutkiewicz, T., J. Konczalik, and M. Przechera; Assessment of the Colorimetric Methods of Determination of Chromium in Air and Urine by Means of Radiosotope Techniques. *Acta. Polon. Pharm. 26:*168 (February 1969).